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Patentanmeldung Nr. Patent application No. Demande de brevet n°

02024808.4

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BASF AKTIENGESELLSCHAFT

67056 Ludwigshafen
ALLEMAGNE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Substituted 6-(2-halogenphenyl)-triazolopyrimidines

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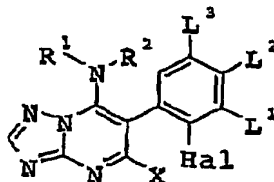
Substituted 6-(2-halogenphenyl)-triazolopyrimidines

Description

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The invention relates to substituted 6-(2-halogenphenyl)-triazolopyrimidines of formula I

10



I

in which

15

R¹ and R² independently denote hydrogen or C₁-C₁₀-alkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, or C₄-C₁₀-alkadienyl, C₁-C₁₀-haloalkyl, C₂-C₁₀-haloalkenyl, C₃-C₁₀-cycloalkyl, phenyl, naphthyl, or

20

a 5- or 6-membered saturated, unsaturated, or aromatic heterocycle, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom,

25

wherein R¹ and R² radicals may be unsubstituted or partly or fully halogenated or may carry one to three groups R^a,

30

R^a is cyano, nitro, hydroxyl, C₁-C₆-alkyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-alkylthio, C₁-C₆-alkylamino, di-C₁-C₆-alkylamino, C₂-C₆-alkenyl, C₂-C₆-alkenyloxy, C₂-C₆-alkynyl, C₃-C₆-alkynyloxy, or C₁-C₄-alkylenedioxy; or

35

R¹ and R² together with the interjacent nitrogen atom represent a 5- or 6-membered heterocycle, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which ring may be substituted by one to three R^a radicals;

40 Hal is halogen;

L¹, L³ independently denote hydrogen, halogen, or C₁-C₄-alkyl;

45

L² is hydrogen, halogen, C₁-C₄-haloalkyl, or NH₂, NHR^b, or N(R^b)₂,

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R^b is C₁-C₈-alkyl, C₃-C₁₀-alkenyl, C₃-C₁₀-alkynyl, C₁-C₆-haloalkyl, C₃-C₆-haloalkenyl, C₃-C₆-haloalkynyl, C₁-C₈-alkoxy-C₁-C₈-alkyl, C₁-C₈-alkylthio-C₁-C₈-alkyl, C₃-C₁₀-cycloalkyl, or C(=O)-A, in which

5

A is hydrogen, hydroxy, C₁-C₈-alkyl, C₁-C₈-alkoxy, C₁-C₆-halogenalkoxy, C₁-C₈-alkylamino or di-(C₁-C₈-alkyl)amino;

10 wherein at least one from L¹, L², and L³ is not hydrogen;

X is halogen, cyano, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy or C₃-C₈-alkenyloxy.

15 Moreover, the invention relates to processes for their preparation, compositions containing them and to their use for combating phytopathogenic fungi.

6-Phenyl-7-amino-triazolopyrimidines are generally known from 20 US 4,567,262, and EP-A 550 113.

Triazolopyrimidines with a trifluorophenyl group in 6-position are disclosed in WO-A 98/46607 and EP-A 945 453. From EP-A 834 513 diverse 6-pentafluorophenyl-triazolopyrimidines are 25 known.

The compounds disclosed in the documents discussed above are said to be active against various phytopathogenic fungi.

30 It is an object of the present invention to provide compounds having improved fungicidal activity.

We have found that this object is achieved by the compounds defined at the outset. Furthermore, we have found processes for their 35 preparation, compositions comprising them and methods for controlling phytopathogenic fungi using the compounds I.

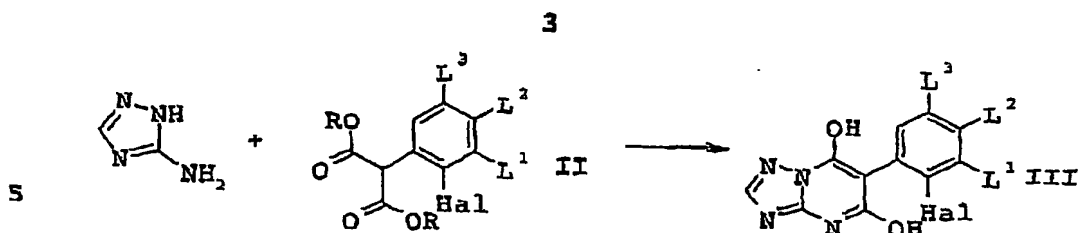
The compounds of formula I differ from the compounds known from closest prior art EP-A 945 453 and EP-A 834 513 in the 2-halogen- 40 phenyl group, which is further substituted, and wherein the 6-position is not substituted.

Compounds of formula I can be prepared similar to the conditions known from EP-A 550 113. Preferably the preparation of compounds 45 of formula I as defined above comprises reacting 5-amino-triazole with 2-(2-halogenphenyl)-substituted malonic acid ester of formula II, in which

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R represents alkyl, preferably C₁-C₆-alkyl, in particular methyl or ethyl, under alkaline conditions, preferably using high boiling tertiary amines as for example tri-n-butylamine as disclosed
10 for example by EP-A 770 615 to yield compounds of formula III.

The resulting 5,7-dihydroxy-6-phenyl-triazolopyrimidine of formula III, wherein L¹ to L³ are as defined for formula I, is subsequently treated with a halogenating agent, preferably with a brominating or chlorinating agent, such as phosphorus oxybromide or
15 phosphorus oxychloride, neat or in the presence of a solvent to give IV, wherein Y is halogen, such as chlorine or bromine.



The reaction is suitably carried out at a temperature in the
25 range from 0°C to 150°C, the preferred reaction temperature being from 80°C to 125°C as disclosed for example by EP-A 770 615.

Dihalo-triazolopyrimidine IV is further reacted with an amine of formula V
30



in which R¹ and R² are as defined in formula I to produce compounds of formula I in which X is halogen.
35

The reaction between the 5,7-dihalo compound IV and the amine of formula V can be carried out under conditions known from WO-A 98/46608. The reaction is preferably carried out in the presence
40 of a solvent. Suitable solvents include ethers, such as dioxane, diethyl ether and, especially, tetrahydrofuran, halogenated hydrocarbons such as dichloromethane and aromatic hydrocarbons, for example toluene.

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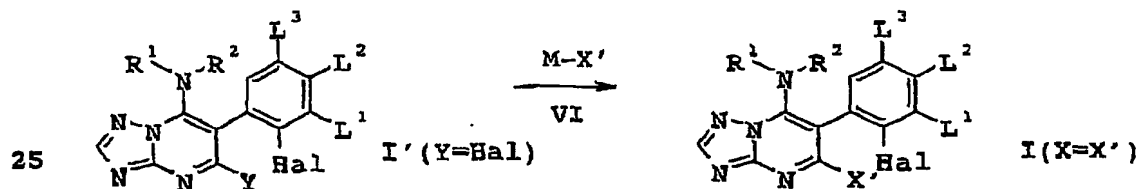
The reaction is suitably carried out at a temperature in the range from 0°C to 70°C, the preferred reaction temperature being from 10°C to 35°C.

5 It is also preferred that the reaction is carried out in the presence of a base. Suitable bases include tertiary amines, such as triethylamine, and inorganic bases, such as potassium carbonate or sodium carbonate. Alternatively, an excess of the compound of formula V may serve as a base.

10

Compounds of formula I in which X denotes cyano, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy or C₃-C₈-alkenyloxy can be prepared by reacting compounds I' in which Y is halogen, preferably chloro, with com-

15 to be introduced to yield formula I compounds, an anorganic cyano salt, an alkoxylate, haloalkoxylate or an alkenyloxylate, respectively, preferably in the presence of a solvent. The cation M in formula VI has minor influence; for practical and economical reasons usually ammonium-, tetraalkylammonium- or alkalimetal- and
20 earth metal salts are preferred.



The reaction is suitably carried out at a temperature in the range from 0 to 120°C, the preferred reaction temperature being from 10 to 40°C [cf. J. Heterocycl. Chem.-Vol.12, p. 861-863

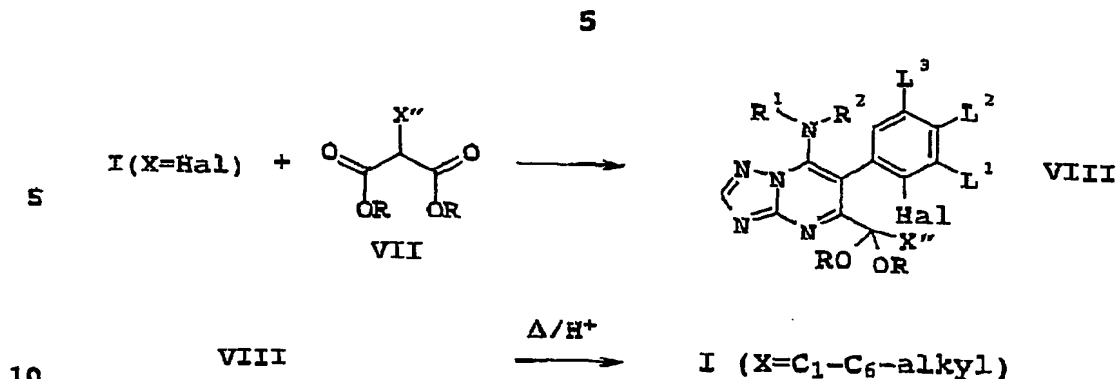
30 (1975)].

Suitable solvents include ethers, such as dioxane, diethyl ether and, especially, tetrahydrofuran, halogenated hydrocarbons such as dichloromethane and aromatic hydrocarbons, for example to-

35 luene.

Compounds of formula I in which X denotes C₁-C₆-alkyl can be prepared by reacting compounds I in which X is halogen, preferably chloro, with malonic acid esters of formula VII, wherein X'' denotes H or C₁-C₅-alkyl and R denotes C₁-C₄-alkyl, to compounds of
40 formula VIII and decarboxylation under conditions described in US 5,994,360.

45



Accordingly, the invention relates to the novel intermediates of formulae II, III and IV.

- 15 The compounds of formula II are preferably prepared by reaction of the corresponding substituted bromobenzenes with sodium dialkylmalonates in the presence of a copper(I) salt [cf. Chemistry Letters, pp. 367-370, 1981; EP-A 10 02 788].
- 20 The compounds of formula II may also be prepared by reaction of an alkyl 2-(2-halogenphenyl)-acetate with dialkylcarbonate in the presence of a strong base, preferably sodium ethoxide and sodium hydride (cf. Heterocycles, pp. 1031-1047, 1996).
- 25 The substituted phenylacetates which are the starting compounds for compounds of formula II are known and commercially available, and/or they are obtainable by generally known methods.

The reaction mixtures are worked up in a customary manner, for example by mixing with water, phase separation and, if required, chromatographic purification of the crude products. Some of the end products are obtained in the form of colorless or slightly brownish, viscous oils, which are purified or freed from volatile components under reduced pressure and at moderately elevated temperatures. If the end products are obtained as solids, purification can also be carried out by recrystallization or digestion.

If individual compounds I are not obtainable by the routes described above, they can be prepared by derivatization of other compounds I.

In the symbol definitions given in the formulae above, collective terms were used which generally represent the following substituents:

- halogen: fluorine, chlorine, bromine and iodine;

6

- C₁-C₁₀-alkyl: saturated, straight-chain or branched hydrocarbon radicals having 1 to 10, especially 1 to 6 carbon atoms, for example C₁-C₄-alkyl as mentioned above or pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, 5 hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 10 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl;
- C₂-C₁₀-alkenyl: unsaturated, straight-chain or branched hydrocarbon radicals having 2 to 10, especially 2 to 6 carbon atoms and a double bond in any position, for example ethenyl, 15 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl and 2-methyl-2-propenyl;
- C₂-C₁₀-alkynyl: straight-chain or branched hydrocarbon radicals 20 having 2 to 10, especially 2 to 4 carbon atoms and a triple bond in any position, for example ethynyl, 1-propynyl, 2-propynyl, 1-butyne, 2-butyne, 3-butyne and 1-methyl-2-propynyl;
- C₃-C₁₀-cycloalkyl: mono- or bicyclic cycloalkyl groups having 3 to 25 10 carbon atoms; monocyclic groups preferably have 3 to 8, especially 3 to 6 ring members, bicyclic groups preferably have 8 to 10 ring members.
- A 5- or 6-membered saturated heterocycle, containing one to four 30 nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, preferably one oxygen atom, for example 1-pyrimidinyl, 2-pyrimidinyl, morpholin-4-yl.
- A 5-membered aromatic heterocycle, containing one to four 35 nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom: 5-membered heteroaryl groups which, in addition to carbon atoms, may contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom as ring members, for example 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 40 2-pyrrolyl, 3-pyrrolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl and 1,3,4-triazol-2-yl; 45

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6-membered aromatic heterocycle, containing one to four nitrogen atoms: 6-membered heteroaryl groups which, in addition to carbon atoms, may contain one to three or one to four nitrogen atoms as ring members, for example 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl and 1,2,4-triazin-3-yl, preferably pyridyl, pyrimidyl, pyrazolyl or thienyl.

With respect to their intended use, preference is given to triazolopyrimidines of the formula I having the following substituents, where the preference is valid in each case on its own or in combination:

A preferred cycloalkyl moiety is cyclopentyl being optionally substituted by one or more nitro, cyano, C₁-C₆-alkyl, C₁-C₆-alkoxy groups.

Preference is given to compounds of formula I in which any alkyl or haloalkyl part of the groups R¹ or R², which may be straight chained or branched, contains up to 10 carbon atoms, preferably 1 to 9 carbon atoms, more preferably 2 to 6 carbon atoms, any alkenyl or alkynyl part of the substituents R¹ or R² contains up to 10 carbon atoms, preferably 2 to 9 carbon atoms, more preferably 3 to 6 carbon atoms, any cycloalkyl part of the substituents R¹ or R² contains from 3 to 10 carbon atoms, preferably from 3 to 8 carbon atoms, more preferably from 3 to 6 carbon atoms, and any bicycloalkyl part of the substituents R¹ or R² contains from 5 to 9 carbon atoms, preferably from 7 to 9 carbon atoms. Any alkyl, alkenyl or alkynyl group may be linear or branched.

Likewise, preference is given to compounds of formula I wherein R¹ is not hydrogen.

Compounds of formula I are preferred in which R¹ represents a straight-chained or branched C₁-C₁₀-alkyl, in particular a branched C₃-C₁₀-alkyl group, a C₃-C₈-cycloalkyl, a C₅-C₉-bicycloalkyl, a C₃-C₈-cycloalkyl-C₁-C₆-alkyl, C₁-C₁₀-alkoxy-C₁-C₆-alkyl, a C₁-C₁₀-haloalkyl or a phenyl group being optionally substituted by one to three halogen atoms or C₁-C₁₀-alkyl or C₁-C₁₀-alkoxy groups.

Moreover, particular preference is given to compounds I in which R¹ and R² together with the interjacent nitrogen atom form an optionally substituted heterocyclic ring, preferably an optionally substituted C₃-C₇-heterocyclic ring, in particular pyrrolidine, piperidine, morpholine, or tetrahydropyridine, wherein the hete-

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rocycle is optionally substituted by one or more C₁-C₄-alkyl or C₁-C₂-haloalkyl groups, preferably by one or two methyl groups.

Particular preference is given to compounds I in which R² represents hydrogen, C₁-C₁₀-alkyl or C₁-C₁₀-haloalkyl, in particular hydrogen.

Moreover, particular preference is given to compounds I in which R² is methyl or ethyl.

10

If R¹ denotes C₁-C₁₀-haloalkyl, preferably polyfluorinated alkyl, in particular 2,2,2-trifluoroethyl, 2-(1,1,1-trifluoropropyl) or 2-(1,1,1-trifluorobutyl), R² preferably represents hydrogen.

15 Particular preference is given to compounds I in which Hal is fluoro, chloro, or bromo, particularly fluoro.

Furthermore, preference is given to compounds I in which L¹ is hydrogen, or fluoro, particularly hydrogen.

20

Besides, particular preference is given to compounds I in which L² is hydrogen, fluoro, trifluoromethyl, amino, dimethylamino, or N-acetylamino, particularly fluoro.

25 Furthermore, preference is given to compounds I in which L² is NHR^b or N(R^b)₂, wherein R^b is methyl or C(=O)-C₁-C₄-alkyl.

Likewise, particular preference is given to compounds I in which L³ is hydrogen, fluoro, methyl, particularly hydrogen.

30

Moreover, preference is given to compounds I in which X is halogen, cyano or methyl, preferably halogen, such as chloro or bromo, particularly chloro.

35 The particularly preferred embodiments of the intermediates with respect to the variables correspond to those of the radicals X, R¹, R², L¹ to L³ of formula I.

Included in the scope of the present invention are (R) and (S) isomers of compounds of general formula I having a chiral center and the racemates thereof, and salts, N-oxides and acid addition compounds.

45 With respect to their use, particular preference is given to the compounds I compiled in the tables below. The groups mentioned in the tables for a substituent are furthermore for their part, in-

dependently of the combination in which they are mentioned, a particularly preferred embodiment of the respective substituents.

Table 1

- 5 Compounds of formula I, in which X is chloro, Hal, L¹ and L³ are fluoro, L² is hydrogen and R¹ and R² correspond to one row in Table A

Table 2

- 10 Compounds of formula I, in which X is cyano, Hal, L¹ and L³ are fluoro, L² is hydrogen and R¹ and R² correspond to one row in Table A

Table 3

- 15 Compounds of formula I, in which X is methyl, Hal, L¹ and L³ are fluoro, L² is hydrogen and R¹ and R² correspond to one row in Table A

Table 4

- 20 Compounds of formula I, in which X is methoxy, Hal, L¹ and L³ are fluoro, L² is hydrogen and R¹ and R² correspond to one row in Table A

Table 5

- 25 Compounds of formula I, in which X is chloro, Hal and L² are fluoro, L¹ and L³ are hydrogen and R¹ and R² correspond to one row in Table A

Table 6

- 30 Compounds of formula I, in which X is cyano, Hal and L² are fluoro, L¹ and L³ are hydrogen and R¹ and R² correspond to one row in Table A

Table 7

- 35 Compounds of formula I, in which X is methyl, Hal and L² are fluoro, L¹ and L³ are hydrogen and R¹ and R² correspond to one row in Table A

Table 8

- 40 Compounds of formula I, in which X is methoxy, Hal and L² are fluoro, L¹ and L³ are hydrogen and R¹ and R² correspond to one row in Table A

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Table 9

Compounds of formula I, in which X is chloro, Hal is fluoro, L¹ and L³ are hydrogen, L² is trifluoromethyl and R¹ and R² correspond to one row in Table A

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Table 10

Compounds of formula I, in which X is cyano, Hal is fluoro, L¹ and L³ are hydrogen, L² is trifluoromethyl and R¹ and R² correspond to one row in Table A

10

Table 11

Compounds of formula I, in which X is methyl, Hal is fluoro, L¹ and L³ are hydrogen, L² is trifluoromethyl and R¹ and R² correspond to one row in Table A

15

Table 12

Compounds of formula I, in which X is methoxy, Hal is fluoro, L¹ and L³ are hydrogen, L² is trifluoromethyl and R¹ and R² correspond to one row in Table A

20

Table 13

Compounds of formula I, in which X is chloro, Hal is fluoro, L¹ and L² are hydrogen, L³ is methyl and R¹ and R² correspond to one row in Table A

25

Table 14

Compounds of formula I, in which X is cyano, Hal is fluoro, L¹ and L² are hydrogen, L³ is methyl and R¹ and R² correspond to one row in Table A

30

Table 15

Compounds of formula I, in which X is methyl, Hal is fluoro, L¹ and L² are hydrogen, L³ is methyl and R¹ and R² correspond to one row in Table A

35

Table 16

Compounds of formula I, in which X is methoxy, Hal is fluoro, L¹ and L² are hydrogen, L³ is methyl and R¹ and R² correspond to one row in Table A

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Table 17

Compounds of formula I, in which X and Hal are chloro, L¹ and L³ are hydrogen, L² is fluoro and R¹ and R² correspond to one row in Table A

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Table 18

Compounds of formula I, in which X is cyano, Hal is chloro, L¹ and L³ are hydrogen, L² is fluoro and R¹ and R² correspond to one row in Table A

5

Table 19

Compounds of formula I, in which X is methyl, Hal is chloro, L¹ and L³ are hydrogen, L² is fluoro and R¹ and R² correspond to one row in Table A

10

Table 20

Compounds of formula I, in which X is methoxy, Hal is chloro, L¹ and L³ are hydrogen, L² is fluoro and R¹ and R² correspond to one row in Table A

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Table 21

Compounds of formula I, in which X is chloro, Hal is fluoro, L¹ and L³ are hydrogen, L² is chloro and R¹ and R² correspond to one row in Table A

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Table 22

Compounds of formula I, in which X is cyano, Hal is fluoro, L¹ and L³ are hydrogen, L² is chloro and R¹ and R² correspond to one row in Table A

25

Table 23

Compounds of formula I, in which X is methyl, Hal is fluoro, L¹ and L³ are hydrogen, L² is chloro and R¹ and R² correspond to one row in Table A

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Table 24

Compounds of formula I, in which X is methoxy, Hal is fluoro, L¹ and L³ are hydrogen, L² is chloro and R¹ and R² correspond to one row in Table A

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Table 25

Compounds of formula I, in which X is chloro, Hal is fluoro, L¹ and L³ are hydrogen, L² is bromo and R¹ and R² correspond to one row in Table A

40

Table 26

Compounds of formula I, in which X is cyano, Hal is fluoro, L¹ and L³ are hydrogen, L² is bromo and R¹ and R² correspond to one row in Table A

45

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Table 27

Compounds of formula I, in which X is methyl, Hal is fluoro, L¹ and L³ are hydrogen, L² is bromo and R¹ and R² correspond to one row in Table A

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Table 28

Compounds of formula I, in which X is methoxy, Hal is fluoro, L¹ and L³ are hydrogen, L² is bromo and R¹ and R² correspond to one row in Table A

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Table 29

Compounds of formula I, in which X and Hal are chloro, L¹ and L³ are hydrogen, L² is bromo and R¹ and R² correspond to one row in Table A

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Table 30

Compounds of formula I, in which X is cyano, Hal is chloro, L¹ and L³ are hydrogen, L² is bromo and R¹ and R² correspond to one row in Table A

20

Table 31

Compounds of formula I, in which X is methyl, Hal is chloro, L¹ and L³ are hydrogen, L² is bromo and R¹ and R² correspond to one row in Table A

25

Table 32

Compounds of formula I, in which X is methoxy, Hal is chloro, L¹ and L³ are hydrogen, L² is bromo and R¹ and R² correspond to one row in Table A

30

Table 33

Compounds of formula I, in which X, Hal and L² are chloro, L¹ and L³ are hydrogen and R¹ and R² correspond to one row in Table A

35 Table 34

Compounds of formula I, in which X is cyano, Hal and L² are chloro, L¹ and L³ are hydrogen and R¹ and R² correspond to one row in Table A

40 Table 35

Compounds of formula I, in which X is methyl, Hal and L² are chloro, L¹ and L³ are hydrogen and R¹ and R² correspond to one row in Table A

45

13

Table 36

Compounds of formula I, in which X is methoxy, Hal and L² are chloro, L¹ and L³ are hydrogen and R¹ and R² correspond to one row in Table A

5

Table 37

Compounds of formula I, in which X is chloro, Hal and L¹ are fluoro, L² and L³ are hydrogen and R¹ and R² correspond to one row in Table A

10

Table 38

Compounds of formula I, in which X is cyano, Hal and L¹ are fluoro, L² and L³ are hydrogen and R¹ and R² correspond to one row in Table A

15

Table 39

Compounds of formula I, in which X is methyl, Hal and L¹ are fluoro, L² and L³ are hydrogen and R¹ and R² correspond to one row in Table A

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Table 40

Compounds of formula I, in which X is methoxy, Hal and L¹ are fluoro, L² and L³ are hydrogen and R¹ and R² correspond to one row in Table A

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Table 41

Compounds of formula I, in which X is chloro, Hal and L³ are fluoro, L¹ and L² hydrogen and R¹ and R² correspond to one row in Table A

30

Table 42

Compounds of formula I, in which X is cyano, Hal and L³ are fluoro, L¹ and L² hydrogen and R¹ and R² correspond to one row in Table A

35

Table 43

Compounds of formula I, in which X is methyl, Hal and L³ are fluoro, L¹ and L² hydrogen and R¹ and R² correspond to one row in Table A

40

Table 44

Compounds of formula I, in which X is methoxy, Hal and L³ are fluoro, L¹ and L² hydrogen and R¹ and R² correspond to one row in Table A

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Table 45

Compounds of formula I, in which X is chloro, Hal, L² and L³ are fluoro, L¹ is hydrogen and R¹ and R² correspond to one row in Table A

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Table 46

Compounds of formula I, in which X is cyano, Hal, L² and L³ are fluoro, L¹ is hydrogen and R¹ and R² correspond to one row in Table A

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Table 47

Compounds of formula I, in which X is methyl, Hal, L² and L³ are fluoro, L¹ is hydrogen and R¹ and R² correspond to one row in Table A

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Table 48

Compounds of formula I, in which X is methoxy, Hal, L² and L³ are fluoro, L¹ is hydrogen and R¹ and R² correspond to one row in Table A

20

Table 49

Compounds of formula I, in which X is chloro, Hal, L¹ and L² are fluoro, L³ is hydrogen and R¹ and R² correspond to one row in Table A

25

Table 50

Compounds of formula I, in which X is cyano, Hal, L¹ and L² are fluoro, L³ is hydrogen and R¹ and R² correspond to one row in Table A

30

Table 51

Compounds of formula I, in which X is methyl, Hal, L¹ and L² are fluoro, L³ is hydrogen and R¹ and R² correspond to one row in Table A

35

Table 52

Compounds of formula I, in which X is methoxy, Hal, L¹ and L² are fluoro, L³ is hydrogen and R¹ and R² correspond to one row in Table A

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Table 53

Compounds of formula I, in which X is chloro, Hal is bromo, L¹ and L³ are fluoro, L² is hydrogen and R¹ and R² correspond to one row in Table A

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Table 54

Compounds of formula I, in which X is cyano, Hal is bromo, L¹ and L³ are fluoro, L² is hydrogen and R¹ and R² correspond to one row in Table A

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Table 55

Compounds of formula I, in which X is methyl, Hal is bromo, L¹ and L³ are fluoro, L² is hydrogen and R¹ and R² correspond to one row in Table A

10

Table 56

Compounds of formula I, in which X is methoxy, Hal is bromo, L¹ and L³ are fluoro, L² is hydrogen and R¹ and R² correspond to one row in Table A

15

Table 57

Compounds of formula I, in which X is chloro, Hal is fluoro, L¹ and L³ are hydrogen, L² is amino and R¹ and R² correspond to one row in Table A

20

Table 58

Compounds of formula I, in which X is cyano, Hal is fluoro, L¹ and L³ are hydrogen, L² is amino and R¹ and R² correspond to one row in Table A

25

Table 59

Compounds of formula I, in which X is methyl, Hal is fluoro, L¹ and L³ are hydrogen, L² is amino and R¹ and R² correspond to one row in Table A

30

Table 60

Compounds of formula I, in which X is methoxy, Hal is fluoro, L¹ and L³ are hydrogen, L² is amino and R¹ and R² correspond to one row in Table A

35

Table 61

Compounds of formula I, in which X is chloro, Hal is fluoro, L¹ and L³ are hydrogen, L² is methylamino and R¹ and R² correspond to one row in Table A

40

Table 62

Compounds of formula I, in which X is cyano, Hal is fluoro, L¹ and L³ are hydrogen, L² is methylamino and R¹ and R² correspond to one row in Table A

45

16

Table 63

Compounds of formula I, in which X is methyl, Hal is fluoro, L¹ and L³ are hydrogen, L² is methylamino and R¹ and R² correspond to one row in Table A

5

Table 64

Compounds of formula I, in which X is methoxy, Hal is fluoro, L¹ and L³ are hydrogen, L² is methylamino and R¹ and R² correspond to one row in Table A

10

Table 65

Compounds of formula I, in which X is chloro, Hal is fluoro, L¹ and L³ are hydrogen, L² is dimethylamino and R¹ and R² correspond to one row in Table A

15

Table 66

Compounds of formula I, in which X is cyano, Hal is fluoro, L¹ and L³ are hydrogen, L² is dimethylamino and R¹ and R² correspond to one row in Table A

20

Table 67

Compounds of formula I, in which X is methyl, Hal is fluoro, L¹ and L³ are hydrogen, L² is dimethylamino and R¹ and R² correspond to one row in Table A

25

Table 68

Compounds of formula I, in which X is methoxy, Hal is fluoro, L¹ and L³ are hydrogen, L² is dimethylamino and R¹ and R² correspond to one row in Table A

30

Table 69

Compounds of formula I, in which X is chloro, Hal is fluoro, L¹ and L³ are hydrogen, L² is N-acetylamino and R¹ and R² correspond to one row in Table A

35

Table 70

Compounds of formula I, in which X is cyano, Hal is fluoro, L¹ and L³ are hydrogen, L² is N-acetylamino and R¹ and R² correspond to one row in Table A

40

Table 71

Compounds of formula I, in which X is methyl, Hal is fluoro, L¹ and L³ are hydrogen, L² is N-acetylamino and R¹ and R² correspond to one row in Table A

45

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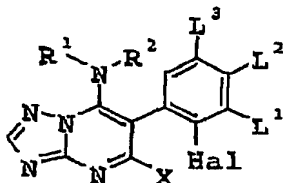
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Table 72

Compounds of formula I, in which X is methoxy, Hal is fluoro, L¹ and L³ are hydrogen, L² is N-acetylamino and R¹ and R² correspond to one row in Table A

5

Table A



I

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No.	R ¹	R ²
A-1	H	H
15 A-2	CH ₂ CH ₃	H
A-3	CH ₂ CH ₃	CH ₃
A-4	CH ₂ CH ₃	CH ₂ CH ₃
A-5	CH ₂ CF ₃	H
20 A-6	CH ₂ CF ₃	CH ₃
A-7	CH ₂ CF ₃	CH ₂ CH ₃
A-8	CH ₂ CCl ₃	H
A-9	CH ₂ CCl ₃	CH ₃
25 A-10	CH ₂ CCl ₃	CH ₂ CH ₃
A-11	CH ₂ CH ₂ CH ₃	H
A-12	CH ₂ CH ₂ CH ₃	CH ₃
A-13	CH ₂ CH ₂ CH ₃	CH ₂ CH ₃
30 A-14	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃
A-15	CH(CH ₃) ₂	H
A-16	CH(CH ₃) ₂	CH ₃
A-17	CH(CH ₃) ₂	CH ₂ CH ₃
A-18	(±) CH(CH ₃)-CH ₂ CH ₃	H
35 A-19	(±) CH(CH ₃)-CH ₂ CH ₃	CH ₃
A-20	(±) CH(CH ₃)-CH ₂ CH ₃	CH ₂ CH ₃
A-21	(S) CH(CH ₃)-CH ₂ CH ₃	H
A-22	(S) CH(CH ₃)-CH ₂ CH ₃	CH ₃
40 A-23	(S) CH(CH ₃)-CH ₂ CH ₃	CH ₂ CH ₃
A-24	(R) CH(CH ₃)-CH ₂ CH ₃	H
A-25	(R) CH(CH ₃)-CH ₂ CH ₃	CH ₃
A-26	(R) CH(CH ₃)-CH ₂ CH ₃	CH ₂ CH ₃
45 A-27	(±) CH(CH ₃)-CH(CH ₃) ₂	H
A-28	(±) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
A-29	(±) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃

18

No.	R ¹	R ²
A-30	(S) CH(CH ₃)-CH(CH ₃) ₂	H
A-31	(S) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
5 A-32	(S) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
A-33	(R) CH(CH ₃)-CH(CH ₃) ₂	H
A-34	(R) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
A-35	(R) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
10 A-36	(±) CH(CH ₃)-C(CH ₃) ₃	H
A-37	(±) CH(CH ₃)-C(CH ₃) ₃	CH ₃
A-38	(±) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
A-39	(S) CH(CH ₃)-C(CH ₃) ₃	H
A-40	(S) CH(CH ₃)-C(CH ₃) ₃	CH ₃
15 A-41	(S) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
A-42	(R) CH(CH ₃)-C(CH ₃) ₃	H
A-43	(R) CH(CH ₃)-C(CH ₃) ₃	CH ₃
A-44	(R) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
20 A-45	(±) CH(CH ₃)-CF ₃	H
A-46	(±) CH(CH ₃)-CF ₃	CH ₃
A-47	(±) CH(CH ₃)-CF ₃	CH ₂ CH ₃
A-48	(S) CH(CH ₃)-CF ₃	H
25 A-49	(S) CH(CH ₃)-CF ₃	CH ₃
A-50	(S) CH(CH ₃)-CF ₃	CH ₂ CH ₃
A-51	(R) CH(CH ₃)-CF ₃	H
A-52	(R) CH(CH ₃)-CF ₃	CH ₃
30 A-53	(R) CH(CH ₃)-CF ₃	CH ₂ CH ₃
A-54	(±) CH(CH ₃)-CCl ₃	H
A-55	(±) CH(CH ₃)-CCl ₃	CH ₃
A-56	(±) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
A-57	(S) CH(CH ₃)-CCl ₃	H
35 A-58	(S) CH(CH ₃)-CCl ₃	CH ₃
A-59	(S) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
A-60	(R) CH(CH ₃)-CCl ₃	H
A-61	(R) CH(CH ₃)-CCl ₃	CH ₃
40 A-62	(R) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
A-63	CH ₂ C(CH ₃)=CH ₂	H
A-64	CH ₂ C(CH ₃)=CH ₂	CH ₃
A-65	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃
45 A-66	cyclopentyl	H
A-67	cyclopentyl	CH ₃
A-68	cyclopentyl	CH ₂ CH ₃

19

No.	R ¹	R ²
A-69		-(CH ₂) ₄ -
A-70		-CH(CH ₃)-(CH ₂) ₃ -
A-71		-CH ₂ CH(CH ₃)(CH ₂) ₂ -
A-72		-(CH ₂) ₅ -
A-73		-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -
A-74		-CH ₂ CH(CH ₃)CH ₂ CH(CH ₃)CH ₂ -

- 10 The compounds I are suitable as fungicides. They have outstanding activity against a broad spectrum of phytopathogenic fungi, in particular from the classes of the *Ascomycetes*, *Deuteromycetes*, *Phycomycetes* and *Basidiomycetes*. Some of them act systemically, and they can be employed in crop protection as foliar- and soil-acting fungicides.

20 They are especially important for controlling a large number of fungi on a variety of crop plants such as wheat, rye, barley, oats, rice, maize, grass, bananas, cotton, soya, coffee, sugar cane, grapevines, fruit species, ornamentals and vegetables such as cucumbers, beans, tomatoes, potatoes and cucurbits, and on the seeds of these plants.

- 25 Specifically, they are suitable for controlling the following plant diseases:

- *Alternaria* species, *Podosphaera* species, *Sclerotinia* species, *Physalospora* canker on vegetables and fruit,
- 30 • *Botrytis cinerea* (gray mold) on strawberries, vegetables, ornamentals and grapevines,
- *Corynespora cassiicola* on cucumbers,
- *Colletotrichum* species on fruit and vegetables,
- *Diplocarpon rosae* on roses,
- 35 • *Elsinoe fawcetti* and *Diaporthe citri* on citrus fruit,
- *Sphaerotheca* species on cucurbits, strawberries and roses,
- *Cercospora* species on peanuts, sugar beets and aubergines,
- *Erysiphe cichoracearum* on cucurbits,
- *Leveillula taurica* on paprika, tomatoes and aubergines,
- 40 • *Mycosphaerella* species on apples and japanese apricot,
- *Phyllactinia kakicola*, *Gloeosporium kaki* on japanese apricot,
- *Gymnosporangium yamadae*, *Leptothyrium pomi*, *Podosphaera leucometriza* and *Gloeodes pomigena* on apples,
- *Cladosporium carpophilum* on pears and japanese apricot,
- 45 • *Phomopsis* species on pears,
- *Phytophthora* species on citrus fruit, potatoes, onions, especially *Phytophthora infestans* on potatoes and tomatoes,
- *Blumeria graminis* (powdery mildew) on cereals,

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- *Fusarium*- and *Verticillium* species on various plants,
- *Glomerella cingulata* on tea,
- *Drechslera*- and *Bipolaris* species on cereals and rice,
- *Mycosphaerella* species on bananas and peanuts,
- 5 • *Plasmopara viticola* on grapevines,
- *Peronospora* species on onions, spinach and chrysanthemum,
- *Phaeoisariopsis vitis* and *Sphaceloma ampelina* on grapefruits,
- *Pseudocercospora herpotrichoides* on wheat and barley,
- *Pseudoperonospora* species on hop and cucumbers,
- 10 • *Puccinia* species and *Typhula* species on cereals and turf,
- *Pyricularia oryzae* on rice,
- *Rhizoctonia* species on cotton, rice and turf,
- *Stagonospora nodorum* and *Septoria tritici* on wheat,
- *Uncinula necator* on grapevines,
- 15 • *Ustilago* species on cereals and sugar cane, and
- *Venturia* species (scab) on apples and pears.

Moreover, the compounds I are suitable for controlling harmful fungi such as *Paecilomyces variotii* in the protection of materials (e.g. wood, paper, paint dispersions, fibers and tissues) and in the protection of stored products.

The compounds I are applied by treating the fungi, or the plants, seeds, materials or the soil to be protected against fungal infection, with a fungicidally active amount of the active ingredients. Application can be effected both before and after infection of the materials, plants or seeds by the fungi.

In general, the fungicidal compositions comprise from 0.1 to 95, preferably 0.5 to 90, % by weight of active ingredient.

When used in crop protection, the rates of application are from 0.01 to 2.0 kg of active ingredient per ha, depending on the nature of the effect desired.

In the treatment of seed, amounts of active ingredient of from 0.001 to 0.1 g, preferably 0.01 to 0.05 g, are generally required per kilogram of seed.

When used in the protection of materials or stored products, the rate of application of active ingredient depends on the nature of the field of application and on the effect desired. Rates of application conventionally used in the protection of materials are, for example, from 0.001 g to 2 kg, preferably 0.005 g to 1 kg, of active ingredient per cubic meter of material treated.

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The compounds I can be converted into the customary formulations, e.g. solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the particular purpose; in any case, it should guarantee a fine and uniform distribution of the compound according to the invention.

The formulations are prepared in a known manner, e.g. by extending the active ingredient with solvents and/or carriers, if desired using emulsifiers and dispersants, it also being possible to use other organic solvents as auxiliary solvents if water is used as the diluent. Auxiliaries which are suitable are essentially: solvents such as aromatics (e.g. xylene), chlorinated aromatics (e.g. chlorobenzenes), paraffins (e.g. mineral oil fractions), alcohols (e.g. methanol, butanol), ketones (e.g. cyclohexanone), amines (e.g. ethanolamine, dimethylformamide) and water; carriers such as ground natural minerals (e.g. kaolins, clays, talc, chalk) and ground synthetic minerals (e.g. highly-disperse silica, silicates); emulsifiers such as non-ionic and anionic emulsifiers (e.g. polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignin-sulfite waste liquors and methylcellulose.

Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutyl-naphthalenesulfonic acid, alkylaryl-sulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates and fatty acids and their alkali metal and alkaline earth metal salts, salts of sulfated fatty alcohol glycol ether, condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol or formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctylphenol, octylphenol, nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignin-sulfite waste liquors and methylcellulose.

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Substances which are suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, e.g. benzene, toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, chloroform, carbon tetrachloride, cyclohexanol, cyclohexanone, chlorobenzene, isophorone, strongly polar solvents, e.g. dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone and water.

Powders, materials for scattering and dusts can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

Granules, e.g. coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active ingredients to solid carriers. Examples of solid carriers are mineral earths, such as silicas, silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, e.g. ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

In general, the formulations comprise of from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active ingredient. The active ingredients are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

The following are exemplary formulations:

- I. 5 parts by weight of a compound according to the invention are mixed intimately with 95 parts by weight of finely divided kaolin. This gives a dust which comprises 5% by weight of the active ingredient.
- II. 30 parts by weight of a compound according to the invention are mixed intimately with a mixture of 92 parts by weight of pulverulent silica gel and 8 parts by weight of paraffin oil which had been sprayed onto the surface of this silica gel. This gives a formulation of the active ingredient with good adhesion properties (comprises 23% by weight of active ingredient).

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- III. 10 parts by weight of a compound according to the invention are dissolved in a mixture composed of 90 parts by weight of xylene, 6 parts by weight of the adduct of 8 to 10 mol of ethylene oxide and 1 mol of oleic acid N-monoethanolamide, 2 parts by weight of calcium dodecylbenzenesulfonate and 2 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil (comprises 9% by weight of active ingredient).
- 5
- IV. 20 parts by weight of a compound according to the invention are dissolved in a mixture composed of 60 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 5 parts by weight of the adduct of 7 mol of ethylene oxide and 1 mol of isooctylphenol and 5 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil (comprises 16% by weight of active ingredient).
- 10
- 15
- V. 80 parts by weight of a compound according to the invention are mixed thoroughly with 3 parts by weight of sodium diisobutyl-naphthalene- α -sulfonate, 10 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 7 parts by weight of pulverulent silica gel, and the mixture is ground in a hammer mill (comprises 80% by weight of active ingredient).
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- VI. 90 parts by weight of a compound according to the invention are mixed with 10 parts by weight of N-methyl- α -pyrrolidone, which gives a solution which is suitable for use in the form of microdrops (comprises 90% by weight of active ingredient).
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- VII. 20 parts by weight of a compound according to the invention are dissolved in a mixture composed of 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 7 mol of ethylene oxide and 1 mol of isooctylphenol and 10 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil. Pouring the solution into 100,000 parts by weight of water and finely distributing it therein gives an aqueous dispersion which comprises 0.02% by weight of the active ingredient.
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- 40
- VIII. 20 parts by weight of a compound according to the invention are mixed thoroughly with 3 parts by weight of sodium diisobutyl-naphthalene- α -sulfonate, 17 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 60 parts by weight of pulverulent silica gel, and the mixture is ground in a hammer mill. Finely distributing
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the mixture in 20,000 parts by weight of water gives a spray mixture which comprises 0.1% by weight of the active ingredient.

- 5 The active ingredients can be used as such, in the form of their formulations or the use forms prepared therefrom, e.g. in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dusts, materials for spreading, or granules, by means of spraying, atomizing, dusting, scattering or pouring. The use forms depend entirely on the intended purposes; in any case, this is intended to guarantee the finest possible distribution of the active ingredients according to the invention.
- 10 15 Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances as such or dissolved in an oil or solvent, can be homogenized in water by means of wetter, tackifier, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.
- 20 25 The active ingredient concentrations in the ready-to-use products can be varied within substantial ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

- The active ingredients may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active ingredient, or even the active ingredient without additives.
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- Various types of oils, herbicides, fungicides, other pesticides, or bactericides may be added to the active ingredients, if appropriate also only immediately prior to use (tank mix). These agents can be admixed with the agents according to the invention in a weight ratio of 1:10 to 10:1.
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- 40 In the use form as fungicides, the compositions according to the invention can also be present together with other active ingredients, e.g. with herbicides, insecticides, growth regulators, fungicides or else with fertilizers. Mixing the compounds I or the compositions comprising them in the use form as fungicides with other fungicides frequently results in a broader fungicidal spectrum of action.
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The following list of fungicides, together with which the compounds according to the invention can be used, is intended to illustrate the possible combinations, but not to impose any limitation:

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sulfur, dithiocarbamates and their derivatives, such as iron(III) dimethyldithiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisdithiocarbamate, manganese ethylenebisdithiocarbamate, manganese zinc ethylenediaminebisdithiocarbamate, tetramethylthiuram disulfide, ammonia complex of zinc (N,N-ethylenebisdithiocarbamate), ammonia complex of zinc (N,N'-propylenebisdithiocarbamate), zinc (N,N'-propylenebisdithiocarbamate), N,N'-polypropylenebis(thiocarbamoyl)disulfide;

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nitro derivatives, such as dinitro(1-methylheptyl)phenyl crotonate, 2-sec-butyl-4,6-dinitrophenyl 3,3-dimethylacrylate, 2-sec-butyl-4,6-dinitrophenylisopropyl carbonate, diisopropyl 5-nitro-isophthalate;

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heterocyclic substances, such as 2-heptadecyl-2-imidazoline acetate, 2,4-dichloro-6-(o-chloroanilino)-s-triazine, O,O-diethyl phthalimidophosphonothioate, 5-amino-1-[bis(dimethylamino)phosphinyl]-3-phenyl-1,2,4-triazole, 2,3-dicyano-1,4-dithioanthraquinone, 2-thio-1,3-dithiolo[4,5-b]quinoxaline, methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, 2-methoxycarbonylaminobenzimidazole, 2-(2-furyl)benzimidazole, 2-(4-thiazolyl)benzimidazole, N-(1,1,2,2-tetrachloroethylthio)tetrahydrophthalimide, N-trichloromethylthiotetrahydrophthalimide, N-trichloromethylthiophthalimide, 5-chloro-2-cyano-4-p-tolyl-imidazole-1-sulfonic acid dimethylamide, N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfo-diamide, 5-ethoxy-3-trichloromethyl-1,2,3-thiadiazole, 2-thiocyanatomethylthiobenzo-thiazole, 1,4-dichloro-2,5-dimethoxybenzene, 4-(2-chlorophenylhydrazono)-3-methyl-5-isoxazolone, pyridine-2-thiol-1-oxide, 8-hydroxyquinoline or its copper salt, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine 4,4-dioxide, 2-methyl-5,6-dihydro-4H-pyran-3-carboxanilide, 2-methylfuran-3-carboxanilide, 2,5-dimethylfuran-3-carboxanilide, 2-Chloro-N-(4'-chloro-biphenyl-2-yl)-nicotinamide, 2,4,5-trimethylfuran-3-carboxanilide, N-cyclohexyl-2,5-dimethylfuran-3-carboxamide, N-cyclohexyl-N-methoxy-2,5-dimethylfuran-3-carboxamide, 2-methylbenzanilide, 2-iodobenzanilide, N-formyl-N-morpholine-2,2,2-trichloroethyl acetal, piperazine-1,4-diylbis-1-(2,2,2-trichloroethyl)formamide, 1-(3,4-dichloroanilino)-1-formylamino-2,2,2-trichloroethane; 2,6-dimethyl-N-tridecylmorpholine or its salts, 2,6-dimethyl-N-cyclododecylmorpholine or its salts, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-cis-2,6-dimethyl-morpholine, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-piperidine,

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- 8-tert.-butyl-1,4-dioxaspiro[4.5]decan-2-ylmethyl(ethyl)(propyl)amine, (RS)-2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-1,2,4-triazole-3-thione, 1-[2-(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole, 1-[2-(2,4-dichlorophenyl)-4-n-propyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole, N-(n-propyl)-N-(2,4,6-trichlorophenoxyethyl)-N'-imidazolyl-urea, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanol, (2RS,3RS)-1-[3-(2-chlorophenyl)-2-(4-fluorophenyl)-oxiran-2-ylmethyl]-1H-1,2,4-triazole, α -(4-chlorophenyl)- α -(1-cyclopropylethyl)-1H-1,2,4-triazole-1-ethanol, α -(2-chlorophenyl)- α -(4-chlorophenyl)-5-pyrimidinemethanol, 5-butyl-2-dimethylamino-4-hydroxy-6-methylpyrimidine, bis(p-chlorophenyl)-3-pyridinemethanol, 1,2-bis(3-ethoxycarbonyl-2-thioureido)benzene, 1,2-bis(3-methoxycarbonyl-2-thioureido)benzene, strobilurines such as methyl (E)-2-[2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl]-3-methoxyacrylate, (E)-2-(methoxyimino)-N-methyl-2-[α -(2,5-xylyloxy)-o-tolyl]acetamide, {2-[6-(2-chlorophenoxy)-5-fluoropyrimidin-4-yloxy]phenyl}(5,6-dihydro-1,4,2-dioxazin-3-yl)methanone O-methyloxime, methyl (E)-methoxyimino[α -(o-tolyloxy)-o-tolyl]acetate, (E)-2-(methoxyimino)-N-methyl-2-(2-phenoxyphenyl)acetamide, (2E)-2-(methoxyimino)-2-[2-[(3E,5E,6E)-5-(methoxyimino)-4,6-dimethyl-2,8-dioxa-3,7-diazanona-3,6-dien-1-yl]phenyl]-N-methylacetamide, methyl-(E)-3-methoxy-2-[2-[6-(trifluoromethyl)-2-pyridyloxymethyl]phenyl]acrylate, methyl N-(2-[1-(4-chlorophenyl)-1H-pyrazol-3-yloxymethyl]phenyl)(N-methoxy)carbamate, methyl (E)-methoxyimino-[(E)- α -[1-(α,α,α -trifluoro-m-tolyl)ethylideneaminoxyl]-o-tolyl]acetate, anilinopyrimidines such as N-(4,6-dimethylpyrimidin-2-yl)aniline, N-[4-methyl-6-(1-propynyl)pyrimidin-2-yl]-aniline, N-[4-methyl-6-cyclopropylpyrimidin-2-yl]aniline, phenylpyrroles such as 4-(2,2-difluoro-1,3-benzodioxol-4-yl)pyrrole-3-carbonitrile, cinnamamides such as 3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)acryloylmorpholine, 3-(4-fluorophenyl)-3-(3,4-dimethoxyphenyl)acryloylmorpholine, and a variety of fungicides such as dodecylguanidine acetate, 3-[3-(3,5-dimethyl-2-oxycyclohexyl)-2-hydroxyethyl]glutarimide, hexachlorobenzene, methyl N-(2,6-dimethylphenyl)-N-(2-furoyl)-DL-alaninate, DL-N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl)-alanine methyl ester, N-(2,6-dimethylphenyl)-N-chloroacetyl-D,L-2-amino-butylolactone, DL-N-(2,6-dimethylphenyl)-N-(phenylacetyl)alanine methyl ester, 5-methyl-5-vinyl-3-(3,5-dichlorophenyl)-2,4-dioxo-1,3-oxazolidine, 3-[3,5-dichlorophenyl(5-methyl-5-methoxymethyl)-1,3-oxazolidi-

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- ne-2,4-dione, 3-(3,5-dichlorophenyl)-1-isopropylcarbamoylhydantoin, N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide, 2-cyano-[N-(ethylaminocarbonyl)-2-methoximino]acetamide, 3,5-Dichloro-N-(3-chloro-1-ethyl-1-methyl-2-oxo-propyl)-4-methyl-benzamide, 1-(3-Bromo-6-methoxy-2-methyl-phenyl)-1-(2,3,4-trimethoxy-6-methyl-phenyl)-methanone, 1-[2-(2,4-dichloro-phenyl)pentyl]-1H-1,2,4-triazole, 2,4-difluoro- α -(1H-1,2,4-triazolyl-1-methyl)benzhydryl alcohol, N-(3-chloro-2,6-dinitro-4-trifluoromethylphenyl)-5-trifluoromethyl-3-chloro-2-aminopyridine, 1-((bis(4-fluorophenyl)methylsilyl)methyl)-1H-1,2,4-triazole, isopropyl 2-methyl-1-[(1-p-tolylethyl)carbamoyl]-(S)-propylcarbamate, [(S)-1-[(1R)-1-(6-fluoro-1,3-benzothiazol-2-yl)ethyl]carbamoyl]-2-methylpropyl]carbamic acid, 6-iodo-2-propoxy-3-propylquinazolin-4(3H)-one.

Synthesis Examples

- With due modification of the starting compounds, the protocols shown in the synthesis examples below were used for obtaining further compounds I. The resulting compounds I, together with physical data, are listed in the Table I which follows.

- Example 1 Preparation of diethyl (2,3,5-trifluorophenyl)-malonate

- Ethyl 2-(2,3,5-trifluorophenyl)-acetate (29 g) was slowly added to a mixture of diethylcarbonate (63 g) and sodium hydride (9.5 g) in toluene (350 ml). After being refluxed for 3 hours, the reaction mixture was cooled, treated with ice-water and washed with water. The organic layer was separated, dried and filtered. The filtrate was concentrated in vacuo to yield 32 g of the title compound.

- Example 2 Preparation of 5,7-dihydroxy-6-(2,3,5-trifluorophenyl)-[1,2,4]-triazolo-[1,5-a]pyrimidine

- A mixture of 3-amino-1,2,4-triazole (14 g), diethyl (2,3,5-trifluorophenyl)-malonate (0.17 mol, obtained from Ex. 1) and tributylamine (50 ml) was heated at 180°C for six hours. The reaction mixture was cooled to about 70°C. After addition of aqueous sodium hydroxide (21 g/200 ml H₂O) the reaction mixture was stirred for 30 minutes. After separation of the organic phase the aqueous phase was extracted with diethyl ether. The aqueous phase was acidified with concentrated hydrochloric acid. The precipitate

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was collected by filtration and dried to yield 43 g of the title compound.

- Example 3 Preparation of 5,7-dichloro-6-(2,3,5-trifluorophenyl)-[1,2,4]-triazolo-[1,5-a]pyrimidine

A mixture of 5,7-dihydroxy-6-(2,3,5-trifluorophenyl)-[1,2,4]-triazolo-[1,5-a]pyrimidine (30 g, obtained from Ex. 2) and phosphorous oxychloride (50 ml) is refluxed for 8 h. Phosphorous oxychloride partly distilled off. The residue was poured into a mixture of dichloromethane and water. The organic layer was separated, dried and filtered. The filtrate was concentrated in vacuo to yield 26 g of the title compound of mp. 191°C.

- Example 4 Preparation of 5-chloro-6-(2,3,5-trifluorophenyl)-7-isopropylamino-[1,2,4]-triazolo[1,5-a]pyrimidine [I-2]

A mixture of isopropylamine (1.5 mmol), triethylamine (1.5 mmol) and dichloromethane (10 ml) was added to a mixture of 5,7-dichloro-6-(2,3,5-trifluorophenyl)-[1,2,4]-triazolo[1,5-a]pyrimidine (1.5 mmol, obtained from Ex. 3) and dichloromethane (20 ml) under stirring. The reaction mixture was stirred for 16 h. at 20 to 25°C and washed with 5% hydrochloric acid. The organic layer was separated, dried and filtered. The filtrate was evaporated and the residue was purified by column chromatography to yield 0.42 g of the title compound of mp. 151°C.

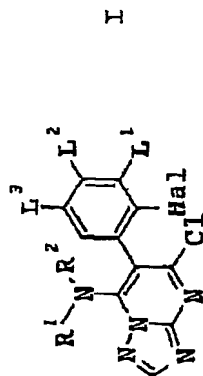
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Table I



No.	R ¹	R ²	Hal	L ¹	L ²	L ³	phys. data (m.p. [°C])
I-1	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	F	F	H	F	128
I-2	CH(CH ₃) ₂	H	F	F	H	F	151
I-3	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		F	F	H	F	171
I-4	cyclopentyl	H	F	F	H	F	111
I-5	CH ₂ CH ₃	CH ₂ CH ₃	F	F	H	F	165
I-6	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	F	F	H	F	107
I-7	CH(CH ₃) ₂	CH ₃	F	F	H	F	172
I-8	(±) CH(CH ₃)-CH ₂ CH ₃	H	F	F	H	F	99
I-9	(S) CH(CH ₃)-CH ₂ CH ₃	H	F	F	H	F	94
I-10	(R) CH(CH ₃)-CH ₂ CH ₃	H	F	F	H	F	94
I-11	(±) CH(CH ₃)-CH(CH ₃) ₂	H	F	F	H	F	113 / 114
I-12	(S) CH(CH ₃)-CH(CH ₃) ₂	H	F	F	H	F	108 / 122
I-13	(R) CH(CH ₃)-CH(CH ₃) ₂	H	F	F	H	F	108 / 122
I-14	(±) CH(CH ₃)-C(CH ₃) ₃	H	F	F	H	F	138 / 129

No.	R ¹	R ²	Hal	L ¹	L ²	L ³	phys. data (m.p. (°C))
I-15	(S) CH(CH ₃)-C(CH ₃) ₃	H	F	F	H	F	129 / 121
I-16	(R) CH(CH ₃)-C(CH ₃) ₃	H	F	F	H	F	129 / 121
I-17	(±) CH(CH ₃)-CF ₃	H	F	F	H	F	164
I-18	(S) CH(CH ₃)-CF ₃	H	F	F	H	F	147
I-19	(R) CH(CH ₃)-CF ₃	H	F	F	H	F	147
I-20	CH ₂ CF ₃	H	F	F	H	F	161
I-21	H	H	F	F	H	F	271
I-22	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	F	H	F	H	105
I-23	CH(CH ₃) ₂	H	F	H	F	H	159
I-24	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -	-(CH ₂) ₂ -	F	H	F	H	208
I-25	(±) CH(CH ₃)-CH ₂ CH ₃	H	F	H	F	H	86
I-26	(±) CH(CH ₃)-C(CH ₃) ₃	H	F	H	F	H	160
I-27	(±) CH(CH ₃)-CF ₃	H	F	H	F	H	151
I-28	(S) CH(CH ₃)-CF ₃	H	F	H	F	H	116
I-29	CH ₂ CF ₃	H	F	H	F	H	181
I-30	CH(CH ₃) ₂	H	F	H	Bz	H	83
I-31	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -	-(CH ₂) ₂ -	F	H	Bz	H	175
I-32	cyclopentyl	H	F	H	Bz	H	161
I-33	CH ₂ CH ₃	CH ₂ CH ₃	F	H	Bz	H	142
I-34	(±) CH(CH ₃)-CH ₂ CH ₃	H	F	H	Bz	H	81
I-35	(±) CH(CH ₃)-C(CH ₃) ₃	H	F	H	Bz	H	196

No.	R ¹	R ²	Hal	L ¹	L ²	L ³	phys. data (m.p. [°C])
I-36	(±) CH(CH ₃)-CF ₃	H	F	H	Br	H	157
I-37	CH ₂ CF ₃	H	F	H	Br	H	108
I-38	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	F	F	H	H	116
I-39	CH(CH ₃) ₂	H	F	F	H	H	130
I-40	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		F	F	H	H	208
I-41	cyclopentyl	H	F	F	H	H	65
I-42	CH ₂ CH ₃	CH ₂ CH ₃	F	F	H	H	135
I-43	(±) CH(CH ₃)-C(CH ₃) ₃	H	F	F	H	H	140
I-44	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	F	H	H	F	121
I-45	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		F	H	H	F	181
I-46	(±) CH(CH ₃)-CH ₂ CH ₃	H	F	H	H	F	134
I-47	(±) CH(CH ₃)-C(CH ₃) ₃	H	F	H	H	F	184
I-48	H	H	F	H	H	F	307
I-49	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	F	H	F	F	138
I-50	CH(CH ₃) ₂	H	F	H	F	F	138
I-51	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		F	H	F	F	192
I-52	cyclopentyl	H	F	H	F	F	165
I-53	(±) CH(CH ₃)-C(CH ₃) ₃	H	F	H	F	F	149
I-54	(±) CH(CH ₃)-CF ₃	H	F	H	F	F	159
I-55	CH ₂ CF ₃	H	F	H	F	F	178
I-56	CH(CH ₃) ₂	H	F	F	F	H	139

No.	R ¹	R ²	Hal	L ¹	L ²	L ³	phys. data (m.p. [°C])
I-57	$-(CH_2)_2CH(CH_3)(CH_2)_2-$	-	F	F	F	H	241
I-58	CH ₂ CH ₃	CH ₂ CH ₃	F	F	F	H	152
I-59	(±) CH(CH ₃)-CH ₂ CH ₃	H	F	F	F	H	123
I-60	(±) CH(CH ₃)-C(CH ₃) ₃	H	F	F	F	H	160
I-61	(±) CH(CH ₃)-CF ₃	H	F	F	F	H	157
I-62	CH ₂ CF ₃	H	F	F	F	H	174
I-63	$-(CH_2)_2CH(CH_3)(CH_2)_2-$	-	F	H	NH ₂	H	249
I-64	(±) CH(CH ₃)-CF ₃	H	F	H	NH ₂	H	196
I-65	$-(CH_2)_2CH(CH_3)(CH_2)_2-$	-	F	H	N(CH ₃) ₂	H	143
I-66	(±) CH(CH ₃)-CF ₃	H	F	H	N(CH ₃) ₂	H	147
I-67	$-(CH_2)_2CH(CH_3)(CH_2)_2-$	-	F	H	NHCOCH ₃	H	135
I-68	(±) CH(CH ₃)-CF ₃	H	F	H	NHCOCH ₃	H	147
I-69	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	Br	F	H	F	139
I-70	CH(CH ₃) ₂	H	Br	F	H	F	138
I-71	$-(CH_2)_2CH(CH_3)(CH_2)_2-$	-	Br	F	H	F	153
I-72	cyclopentyl	H	Br	F	H	F	117
I-73	(±) CH(CH ₃)-CH ₂ CH ₃	H	Br	F	H	F	121
I-74	(S) CH(CH ₃)-CH ₂ CH ₃	H	Br	F	H	F	133
I-75	(R) CH(CH ₃)-CH ₂ CH ₃	H	Br	F	H	F	133
I-76	(±) CH(CH ₃)-CH(CH ₃) ₂	H	Br	F	H	F	113
I-77	(S) CH(CH ₃)-CH(CH ₃) ₂	H	Br	F	H	F	125

No.	R ¹	R ²	Hal	L ¹	L ²	L ³	phys. data (m.p. [°C])
I-78	(R) CH(CH ₃)-CH(CH ₃) ₂	H	Br	F	H	F	125
I-79	(±) CH(CH ₃)-C(CH ₃) ₃	H	Br	F	H	F	119
I-80	(S) CH(CH ₃)-C(CH ₃) ₃	H	Br	F	H	F	130
I-81	(R) CH(CH ₃)-C(CH ₃) ₃	H	Br	F	H	F	130
I-82	(±) CH(CH ₃)-CF ₃	H	Br	F	H	F	65
I-83	(S) CH(CH ₃)-CF ₃	H	Br	F	H	F	78
I-84	(R) CH(CH ₃)-CF ₃	H	Br	F	H	F	78
I-85	H	H	Br	F	H	F	278
I-86	(S) CH(CH ₃)-CH ₂ CH ₃	H	F	H	F	H	79
I-87	(R) CH(CH ₃)-CH ₂ CH ₃	H	F	H	F	H	79
I-88	(S) CH(CH ₃)-CH(CH ₃) ₂	H	F	H	F	H	133
I-89	(R) CH(CH ₃)-CH(CH ₃) ₂	H	F	H	F	H	133
I-90	(S) CH(CH ₃)-C(CH ₃) ₃	H	F	H	F	H	161
I-91	(R) CH(CH ₃)-C(CH ₃) ₃	H	F	H	F	H	161
I-92	(R) CH(CH ₃)-CF ₃	H	F	H	F	H	116
I-93	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	F	H	Cl	H	123
I-94	(±) CH(CH ₃)-CH ₂ CH ₃	H	F	H	Cl	H	110
I-95	(S) CH(CH ₃)-CH ₂ CH ₃	H	F	H	Cl	H	99
I-96	(R) CH(CH ₃)-CH ₂ CH ₃	H	F	H	Cl	H	99
I-97	(±) CH(CH ₃)-CH(CH ₃) ₂	H	F	H	Cl	H	141
I-98	(S) CH(CH ₃)-CH(CH ₃) ₂	H	F	H	Cl	H	131

No.	R ¹	R ²	Hal	L ¹	L ²	L ³	phys. data (m.p. [°C])
I-99	(R) CH(CH ₃)-CH(CH ₃) ₂	H	F	H	Cl	H	131
I-100	(±) CH(CH ₃)-C(CH ₃) ₃	H	F	H	Cl	H	191
I-101	(S) CH(CH ₃)-C(CH ₃) ₃	H	F	H	Cl	H	186
I-102	(R) CH(CH ₃)-C(CH ₃) ₃	H	F	H	Cl	H	185
I-103	(±) CH(CH ₃)-CF ₃	H	F	H	Cl	H	162
I-104	(S) CH(CH ₃)-CF ₃	H	F	H	Cl	H	162
I-105	(R) CH(CH ₃)-CF ₃	H	F	H	Cl	H	162
I-106	CH ₂ CF ₃	H	F	H	Cl	H	146

In some cases of chiral groups R¹ and due to the hindered rotation of the phenyl group two diastereomers exist which may differ in their physical properties.

Examples of the action against harmful fungi

The fungicidal action of the compounds of the formula I was demonstrated by the following experiments:

The active compounds, separately or together, were formulated as a 10% emulsion in a mixture of 70% by weight of cyclohexanone, 20% by weight of Nekanil® LN (Lutensol® AP6, wetting agent having emulsifying and dispersant action based on ethoxylated alkylphenols) and 10% by weight of Wettol® EM (nonionic emulsifier based on ethoxylated castor oil) and diluted with water to the desired concentration.

15 Use Example 1 - Fungicidal control of early blight on tomatoes (*Alternaria solani*)

Leaves of pot grown tomato seedlings of the "Große Fleischtomate St. Pierre" variety were sprayed with an aqueous suspension containing the active compound in the concentration mentioned below prepared from a stock solution consisting of 10 % of the active ingredient in a mixture of 70% of cyclohexanone, 20% wetting agent, and 10% of emulsifier. The next day the leaves were infected with a zoospore suspension of *Alternaria solani* (0.17×10^6 spores per ml of a 2% strength biomalt solution). The plants were then placed in a water vapour-saturated chamber at 20 to 22°C. After 5 days the disease had spread to such a great extent on the untreated plants that the fungicidal activity of the substances could be assessed.

30 In this test, the plants which had been treated with 250 ppm of compounds I-2, I-4, I-8, I-17, and I-20, resp., showed an infection of not more than 7 %, whereas the untreated plants were infected to 90 %.

35 Use Example 2 - Control of gray mould (*Botrytis cinerea*) on paprika leaves

Paprika seedlings were sprayed to run-off at the four- to five leave stage with an aqueous suspension containing the concentration of active ingredient mentioned below, prepared from a stock solution containing 10 % of the active ingredient in a mixture of 70% of cyclohexanone, 20% wetting agent, and 10% of emulsifier. The next day the plants were inoculated with a spore suspension of *Botrytis cinerea* containing 1.7×10^6 spores per ml in 2 wt. % aqueous biomalt solution. The infected plants were then incubated in chambers with high humidity for five days at 22-24°C. The ex-

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tent of fungus spread was assessed as %-attack of the whole leaf surface.

In this test, the plants which had been treated with 250 ppm of 5 compounds I-2, I-4, I-5, I-8, I-17, and I-20, resp., showed an infection of not more than 5 %, whereas the untreated plants were infected to 85 %.

Use Example 3 - Fungicidal control of grape downy mildew (*Plasmopara viticola*)

Leaves of potted vines of the "Müller Thurgau" variety were sprayed with aqueous liquors made from a stock solution containing 10 % of the active ingredient in a mixture of 70% of cyclohexanone, 20% wetting agent, and 10% of emulsifier. The next day 15 they were inoculated with an aqueous spore suspension of *Plasmopara viticola* by spraying it at the lower leaf-side. Then the trial plants were transferred for 48 h to a humid chamber with about 24°C and a relative humidity close to 100 %. For a period of 20 5 days, cultivation followed in a greenhouse at 20 to 30°C. To stimulate the outbreak of the disease symptoms, the plants were transferred to a humid chamber again for 16 hours. Then the extent of fungal attack on the lower leaf surface was visually assessed as % diseased leaf area.

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In this test, the plants which had been treated with 250 ppm of compounds I-2, I-4, I-8, I-17, and I-20, resp., showed an infection of not more than 15 %, whereas the untreated plants were infected to 95 %.

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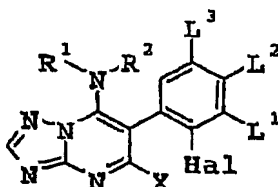
Use Example 4 - Action on *Pyricularia oryzae* (protective action)

Leaves of pot grown rice seedlings of the "Tai-Nong 67" variety were sprayed to runoff with an aqueous suspension, containing the 35 concentration of active ingredient mentioned below, prepared from a stock solution containing 10 % of the active ingredient in a mixture of 70 % cyclohexanone, 20 % wetting agent, and 10 % emulsifier. The next day the plants were inoculated with an aqueous spore suspension of *Pyricularia oryzae*. The plants were then placed for 6 days in a humid chamber at 22 to 24°C and a relative humidity of 95 to 99 %. The extent of fungus spread was assessed as %-attack of the whole leaf surface.

In this test, the plants which had been treated with 250 ppm of 45 compounds I-2, I-4, I-5, and I-20, resp., showed an infection of not more than 15%, whereas the untreated plants were infected to 80 %.

Claims:

1. Substituted 6-(2-halogenphenyl)-triazolopyrimidines of formula I



I

in which

- R^1 and R^2 independently denote hydrogen or C_1 - C_{10} -alkyl, C_2 - C_{10} -alkenyl, C_2 - C_{10} -alkynyl, or C_4 - C_{10} -alkadienyl, C_1 - C_{10} -haloalkyl, C_2 - C_{10} -haloalkenyl, C_3 - C_{10} -cycloalkyl, phenyl, naphthyl, or

- a 5- or 6-membered saturated, unsaturated, or aromatic heterocycle, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom,

- wherein R^1 and R^2 radicals may be unsubstituted or partly or fully halogenated or may carry one to three groups R^a ,

- R^a is cyano, nitro, hydroxyl, C_1 - C_6 -alkyl, C_3 - C_6 -cycloalkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -alkylthio, C_1 - C_6 -alkylamino, di- C_1 - C_6 -alkylamino, C_2 - C_6 -alkenyl, C_2 - C_6 -alkenyloxy, C_2 - C_6 -alkynyl, C_3 - C_6 -alkynyloxy, or C_1 - C_4 -alkylenedioxy; or

- R^1 and R^2 together with the interjacent nitrogen atom represent a 5- or 6-membered heterocycle, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which ring may be substituted by one to three R^a radicals;

- Hal is halogen;

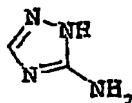
L^1, L^3 independently denote hydrogen, halogen, or C_1 - C_4 -alkyl;

- L^2 is hydrogen, halogen, C_1 - C_4 -haloalkyl, or NH_2 , NHR^b , or $N(R^b)_2$,

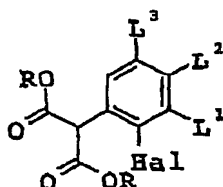
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- 5 R^b is C_1 - C_8 -alkyl, C_3 - C_{10} -alkenyl, C_3 - C_{10} -alkynyl, C_1 - C_6 -haloalkyl, C_3 - C_6 -haloalkenyl, C_3 - C_6 -haloalkynyl, C_1 - C_8 -alkoxy- C_1 - C_8 -alkyl, C_1 - C_8 -alkylthio- C_1 - C_8 -alkyl, C_3 - C_{10} -cycloalkyl, or $C(=O)$ -A, in which
- A is hydrogen, hydroxy, C_1 - C_8 -alkyl, C_1 - C_8 -alkoxy, C_1 - C_6 -halogenalkoxy, C_1 - C_8 -alkylamino or di- $(C_1$ - C_8 -alkyl)amino;
- 10 wherein at least one from L^1 , L^2 , and L^3 is not hydrogen;
- X is halogen, cyano, C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -haloalkoxy or C_3 - C_8 -alkenyloxy.
- 15 2. Compounds of formula I according to claim 1, in which
- R^1 is straight chained or branched C_2 - C_6 -alkenyl, C_1 - C_6 -alkyl, or C_1 - C_{10} -haloalkyl, and
- 20 R^2 is hydrogen or C_1 - C_6 -alkyl, or
- R^1 and R^2 together with the interjacent nitrogen atom represent a heterocyclic ring with 5 or 6 carbon atoms being optionally substituted with one or two C_1 - C_4 -alkyl groups.
- 25
3. Compounds according to claims 1 or 2 in which R^1 and R^2 together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring being optionally substituted
- 30 with one or two methyl groups.
4. Compounds according to claims 1 to 3 in which X is halogen.
5. A process for the preparation of compounds of formula I as defined in claim 4 which comprises reacting
- 35 5-amino-1,2,4-triazole



40 with 2-phenyl-substituted malonic acid ester of formula II,

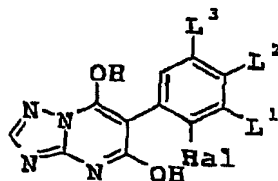


II

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wherein Hal, L¹, L², and L³ are as defined in formula I, and R denotes C₁-C₆-alkyl, under alkaline conditions, to yield compounds of formula III,

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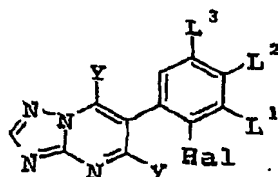


III

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which are subsequently treated with a halogenating agent to give 5,7-dihalo-6-phenyl-triazolopyrimidines of formula IV

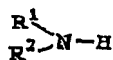
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IV

in which Y is halogen with an amine of formula V

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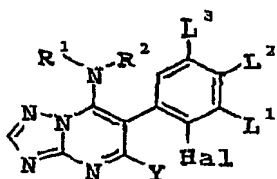
V

in which R¹ and R² are as defined in formula I to produce compounds of formula I.

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6. A process for the preparation of compounds of formula I according to claim 1 wherein X is cyano, C₁-C₁₀-alkoxy, or C₁-C₁₀-haloalkyl, which comprises reacting 5-halogen-triazolopyrimidine of formula I',

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I' (X=Hal)

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wherein Y is halogen, with compounds of formula VI,



VI

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which are, dependent from the value of X' to be introduced, an anorganic cyano salt, an alkoxylate, haloalkoxylate or an alkenyloxylate, resp., wherein M is ammonium-, tetraalkylammonium-, alkalimetal- or earth metal cation, to produce compounds of formula I.

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7. Intermediates of formulae II, III, and IV as defined in claim 5.
8. A composition suitable for controlling phytopathogenic fungi, comprising a solid or liquid carrier and a compound of the formula I as claimed in claim 1.
9. A method for controlling phytopathogenic fungi, which comprises treating the fungi or the materials, plants, the soil or the seed to be protected against fungal attack with an effective amount of a compound of the formula I as claimed in claim 1.

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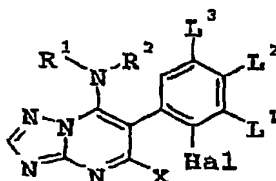
Substituted 6-(2-halogenphenyl)-triazolopyrimidines

Abstract

5

Substituted 6-(2-halogenphenyl)-triazolopyrimidines of formula I

10



I

in which

15 R^1 and R^2 independently denote hydrogen or alkyl, alkenyl, alkynyl, alkadienyl, haloalkyl, haloalkenyl, cycloalkyl, phenyl, naphthyl, or a 5- or 6-membered saturated, unsaturated, or aromatic heterocycle, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, wherein R^1 and R^2 radicals may be

20 substituted as defined in the description, or

R^1 and R^2 together with the interjacent nitrogen atom represent a 5- or 6-membered heterocycle, containing one to four

25 nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which ring may be substituted as defined in the description;

Hal is halogen;

30

L^1, L^3 independently denote hydrogen, halogen, or alkyl;

L^2 is hydrogen, halogen, haloalkyl, or NH_2 , NHR^b , or $N(R^b)_2$, wherein R^b is as defined in the description,

35

wherein at least one from L^1 , L^2 , and L^3 is not hydrogen;

X is halogen, cyano, alkyl, alkoxy, haloalkoxy or alkenyloxy.

40 processes for their preparation, compositions containing them and to their use for combating phytopathogenic fungi.

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